

10 502 504

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 July 2003 (31.07.2003)

PCT

(10) International Publication Number
WO 03/062520 A1

- (51) International Patent Classification⁷: **D06L 1/00**, C11D 11/00
- (21) International Application Number: PCT/NL02/00788
- (22) International Filing Date: 4 December 2002 (04.12.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0275265.5 23 January 2002 (23.01.2002) EP
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/062520 A1

(54) Title: A METHOD OF DRY CLEANING ARTICLES USING DENSIFIED CARBON DIOXIDE

(57) Abstract: The present invention provides a method for the removal of stains from articles, especially fabric, using densified carbon dioxide. More particularly the invention is concerned with a method of dry cleaning an article comprising the successive steps of (a) contacting the article with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60 °C and a pressure between 1 and 100 MPa, so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and (b) separating the article and the fluid dry cleaning composition; wherein the fluid dry cleaning composition comprises an ionic surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in an undissolved solid form. It was surprisingly discovered that the use of an ionic surfactant, e.g. a surfactant that contains a lipophilic alkyl residue and an amine, sulphate, phosphate and/or carboxylate residue, produces exceptionally good cleaning results if said surfactant is employed in an amount that exceeds its maximum solubility in the densified carbon dioxide composition and provided said surfactant is present during the cleaning operation in the form of undissolved solid particles.

A METHOD OF DRY CLEANING ARTICLES USING DENSIFIED CARBON DIOXIDE

TECHNICAL FIELD

The present invention provides a method for the removal of stains from articles, especially fabric, using densified carbon dioxide. More particularly the invention is concerned with a method of dry cleaning an article comprising the successive steps of contacting the article with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa, so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition, and separating the article and the fluid dry cleaning composition, wherein the fluid dry cleaning composition contains a surfactant.

BACKGROUND OF THE INVENTION

Densified, particularly supercritical fluid, carbon dioxide has been suggested as an alternative to halocarbon solvents used in conventional dry cleaning.

Densified carbon dioxide provides a nontoxic, inexpensive, recyclable and environmentally acceptable solvent to remove soils in the dry cleaning process. The supercritical carbon dioxide has been shown to be effective in removing nonpolar stains such as motor oil, when combined with a viscous cleaning solvent, particularly mineral oil or petrolatum as described in U.S. 5,279,615

The solvent power of densified carbon dioxide is low relative to ordinary liquid solvents and the carbon dioxide solvent alone is less effective on hydrophilic stains such as grape juice, coffee and tea and on compound hydrophobic stains such as lipstick and candle wax, unless surfactants and solvent modifiers are added.

A cleaning system combining particular anionic or nonionic surface active agents with supercritical fluid carbon dioxide is described in DE-A 39 04 514. These anionic and nonionic agents, such as alkylenebenzene sulfates and sulfonates, ethoxylated alkylene phenols and ethoxylated fatty alcohols, were particularly effective when combined with a relatively large amount of water (greater than or equal to 4%).

US 5,676,705 describes a method of dry cleaning fabrics comprising contacting stained fabric with a dry cleaning system comprising densified carbon dioxide and 0.001% to 10% by weight of a surfactant compound which is soluble in the densified carbon dioxide. The examples of the US-patent disclose methods wherein the surfactants are deemed to be

fully dissolved during the actual dry cleaning operation. Furthermore these surfactants are liquid under the cleaning conditions employed in these methods.

US 5,858,022 relates to a method for dry cleaning articles in carbon dioxide, comprising: contacting an article to be cleaned with a liquid dry cleaning composition comprising a mixture of carbon dioxide, water, surfactant and an organic co-solvent; and then separating the article from the liquid dry cleaning composition. The methods described in the examples utilise a cleaning composition in which the surfactants are fully dissolved during the cleaning operation.

US 6,200,352 describes a method of dry cleaning articles such as fabrics and clothing with the help of a liquid dry cleaning composition that comprises a mixture of carbon dioxide, a surfactant and an organic co-solvent. The preferred surfactant is one that does not contain a CO₂-philic group.

The dry cleaning systems using densified carbon dioxide known in the art suffer from the drawback that, although they may effectively be used to remove certain types of stains, they are incapable of effectively removing all sorts of stains including nonpolar stains (e.g. those made by a nonpolar organic component such as mineral oil, vegetable oil, sebum etc.), polar stains (e.g. grape juice, coffee and tea stains), compound hydrophobic stains (e.g. stains from lipstick and candle wax) as well as particulate soils (e.g. soils containing insoluble solid components such as silicates, carbon black etc.).

The present invention provides an improved dry cleaning method that utilises densified carbon dioxide and a special surfactant which method offers the advantage that it can be used to effectively remove all sorts of stains from articles such as fabrics.

SUMMARY OF THE INVENTION

The inventors have surprisingly discovered that in a method of dry cleaning articles with a densified carbon dioxide composition, the use of an ionic surfactant, e.g. a surfactant that contains a lipophilic alkyl residue and an amine, sulphate, phosphate and/or carboxylate residue, produces exceptionally good cleaning results if said surfactant is employed in an amount that exceeds its maximum solubility in the densified carbon dioxide composition under the conditions employed during the cleaning operation and provided said surfactant is present during the cleaning operation in the form of undissolved solid particles. It was unexpectedly found that the resulting presence of undissolved ionic surfactant particles makes it possible to effectively remove all sorts of stains, ie. polar, nonpolar, compound stains and in particular particulate soils.

Although the inventors do not wish to be bound by theory it is believed that the exceptionally good results obtained with the present method are partly due to the ability of the ionic surfactant particles to manifest and retain an electrostatic surface charge during the washing operation, allowing these particles to capture and bind soil particles until the resulting aggregates are removed from the cleaned article together with the densified carbon dioxide composition. Thus, the presence of a significant amount of undissolved ionic surfactant particles reinforces the detergent effect of the densified carbon dioxide and the dissolved ionic surfactant.

DETAILED DESCRIPTION OF THE INVENTION

Accordingly the present invention relates a method of dry cleaning an article comprising the successive steps of:

- a) contacting the article with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa, so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and
 - b) separating the article and the fluid dry cleaning composition;
- wherein the fluid dry cleaning composition comprises an ionic surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in an undissolved solid form.

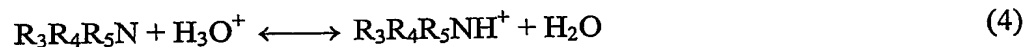
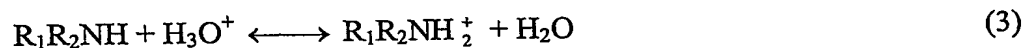
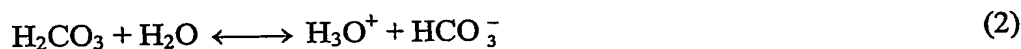
The term "ionic surfactant" as used herein refers to surfactants that are either positively charged (cationic surfactants), negatively charged (anionic surfactants) or zwitterions at the conditions applied in step a).

The term "cleaning" as used herein refers to any removal of soil, dirt, grime, or other unwanted material, whether partial or complete. The present method may be used to clean nonpolar stains, polar stains, compound hydrophobic stains and particulate soils. Examples of articles that can suitably be cleaned by the method of the invention include fabrics such as woven and non-woven fabrics formed from materials such as cotton, wool, silk, leather, rayon, polyester, acetate, fiberglass, furs, etc. These fabrics may have been formed into items such as clothing, work gloves, rags, leather goods (e.g. handbags and brief cases), etc. The present method may also be used to clean non-fabric articles such as semiconductors, micro electromechanical devices, opto electronics, fiber optics and machined or fabricated metal parts.

During the cleaning operation the undissolved surfactant is present in a solid form, especially in the form of solid particles. It is noted that the present method also encompasses the use of surfactants which are liquid at room temperature and atmospheric pressure, but which surfactants form solid particles prior to and/or during step a), e.g. as a result of a chemical or physical interaction with other components present in the cleaning composition. For instance, liquid amine surfactants may suitably be employed in the present process as they form solid particles during the cleaning operation, probably as a result of the reaction with carbon dioxide, resulting in the formation of a solid carbamate.

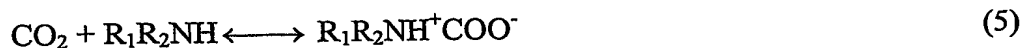
Examples of reactions that may occur between amine surfactants, carbon dioxide and other components of the fluid dry cleaning composition prior to and/or during step a) and which could lead to the formation of reaction products that will precipitate as solid particles include:

Protonation of the amines according to the following reactions [1-4]:

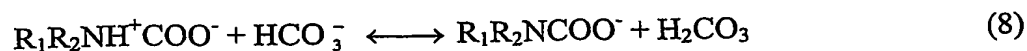
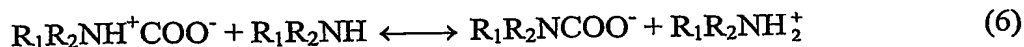


in which $\text{R}_1\text{R}_2\text{NH}$ is a primary or a secondary amine and $\text{R}_3\text{R}_4\text{R}_5\text{N}$ a tertiary amine.

Primary and secondary amines can also react with carbon dioxide to form a zwitterion [5]:



This zwitterion is found in the isoelectric area. Above the isoelectric area, the zwitterion can be deprotonated by a base [6-8]:



Below the isoelectric area of the zwitterion, the zwitterion can be protonated according to the following reaction [9]:



In order to provide sufficient time to allow stains to dissolve and/or to disperse into the dry cleaning fluid it is preferred that the duration of step a) exceeds 1 minute, more preferably 2 minutes, and most preferably 5 minutes.

The results obtained with the present method are very dependent on the type of ionic surfactant used. Very good results are obtained with an ionic surfactant that contains a lipophilic, optionally heterogeneous hydrocarbyl residue with 3-25 carbon atoms and one or more groups selected from amine, phosphate, phosphonate, phosphinate, phosphonite, phosphine, phosphinite, phosphite, quaternary phosphonium salt, quaternary ammonium salt, sulphate, sulphonate, sulphinate, sulphenate, sulphide and carboxylate groups. The aforementioned (polar) groups may be employed in protonated or salt form, e.g. as salts with monovalent cations such as sodium, potassium and ammonium, or as salts with divalent cations such as copper, magnesium, zinc and calcium.

Exceptionally good results can be achieved with an ionic surfactant that is represented by the formula R_1X , XR_1X , R_2YR_2 , $R_3Z(R_3')R_3''$ or $R_3E(R_3')(R_3'')R_3'''D$ wherein:

R_1 is a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkyl; a substituted or unsubstituted, optionally heterogeneous C_3 - C_{16} cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;

R_2 and R_2' independently are R_1 , X , R_aX or $R_a(X)_2$;

R_3 , R_3' , R_3'' and R_3''' independently are R_1 , X , R_aX , YR_1 , $R_a(YR_a)_nYR_1$ or $Y(R_aY)_nR_1$;

R_a is a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkyl; a substituted or unsubstituted, optionally heterogeneous C_3 - C_{16} cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;

and wherein

X is NH_2 , NH_3^+ , $OP(O)(OM_1)(OM_2)$, $OP(O)_3^{2-}Q^{2+}$, $P(O)(OM_1)(OM_2)$, $P(O)_3^{2-}Q^{2+}$,

$P(O)(H)(OM_1)$, $OS(O)_2(OM_1)$, $S(O)_2(OM_1)$, $S(O)(OM_1)$, COO^- or $COOM_1$;

Y is NH , NH_2^+ , $OP(O)(OM_1)O$, $P(O)(OM_1)O$, $P(O)(OM_1)$, $OS(O)_2O$, $S(O)_2O$, $S(O)O$;

Z is N , NH^+ ;

E is N^+ ;

D is F^- , Cl^- , Br^- or I^- ;

M_1 and M_2 independently represent sodium, potassium, ammonium or hydrogen;

Q^{2+} represents Ca^{2+} , Cu^{2+} , Mg^{2+} or Zn^{2+} ; and

$n = 0-20$.

Particularly good results are obtained with the present invention if the ionic surfactant is represented by the formula R_1X , XR_1X , or R_2YR_2' , wherein X is NH_2 , NH_3^+ , $COOM_1$, COO^- , $OP(O)(OM_1)(OM_2)$, $OS(O)_2(OM_1)$ and Y is NH . More preferably X is NH_2 and/or $COOM_1$ and Y is NH .

In another preferred embodiment R_1 is a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3 - C_{22} alkyl, preferably C_8 - C_{22} alkyl or are a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3 - C_{22} alkenyl, preferably C_8 - C_{22} alkenyl. Most preferably, R_1 is an unsubstituted, linear or branched C_3 - C_{22} alkyl, preferably C_8 - C_{22} alkyl or are an unsubstituted, linear or branched C_3 - C_{22} alkenyl, preferably C_8 - C_{22} alkenyl.

In case R_2 or R_2' represents $R_a(X)$ it is preferred that the X -radical is substituted to the terminal carbon atom, i.e. the carbon atom farthest from Y or Z . Similarly, in case R_2 or R_2' represents $R_a(X)_2$ it is preferred that both X -radicals are substituted to the terminal carbon atom. In an even more preferred embodiment in the formula $R_a(X)_2$ one X represents NH_2 or NH_3^+ and the other X represents $COOM_1$ or COO^- .

In yet another preferred embodiment R_a is a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3 - C_{22} alkyl, preferably C_8 - C_{22} alkyl or are a substituted or unsubstituted, linear or branched, optionally heterogeneous C_3 - C_{22} alkenyl, preferably C_8 - C_{22} alkenyl. Most preferably, R_a is an unsubstituted, linear or branched C_3 - C_{22} alkyl, preferably C_8 - C_{22} alkyl or are an unsubstituted, linear or branched C_3 - C_{22} alkenyl, preferably C_8 - C_{22} alkenyl. The liquid dry-cleaning compositions useful for carrying out the present invention typically include some water. The source of the water is not critical in all applications. The water may be added to the dry cleaning composition before the articles to be cleaned are deposited therein, it may be added during the cleaning operation or it can be water carried by or previously added to the garments, etc.

In one embodiment of the invention, better particulate cleaning may be obtained in the absence of water added to the dry-cleaning composition. There is inherently water present on or in the garments or articles to be cleaned as they are placed in the cleaning vessel. The presence of a certain amount of water in a fabric will result in a certain swelling of the fabric which is believed to make the fabric more easily accessible for the dry cleaning composition.

The improved accessibility facilitates the removal of stains (particularly oil and fat stains) that have penetrated into the interior of the fabric.

According to a preferred embodiment of the present method, the fluid dry cleaning composition contains less than 10 wt.% water. More preferably the composition contains less than 6 wt.% water. Even more preferably the water content of the dry cleaning composition is between 0.0001 and 5 wt.%, most preferably the water content is in the range of 0.03-5 wt.%. Here the water content relates to the total water content of the composition, i.e. water that may originate from different sources (e.g. the article) as described above.

In a preferred embodiment of the present method in addition to carbon dioxide one or more co-solvents are employed in the fluid dry cleaning mixture. Suitable examples of such co-solvents include aliphatic and aromatic hydrocarbons, and esters and ethers thereof, particularly mono and di-esters and ethers (e.g., EXXON ISOPAR L, ISOPAR M, ISOPAR V, EXXON EXXSOL, EXXON DF 2000, CONDEA VISTA LPA-170N, CONDEA VISTA LPA-210, cyclohexanone, and dimethyl succinate), alkyl and dialkyl carbonates (e.g., dimethyl carbonate, dibutyl carbonate, di-t-butyl dicarbonate, ethylene carbonate, and propylene carbonate), alkylene and polyalkylene glycols, and ethers and esters thereof (e.g., ethylene glycol-n-butyl ether, diethylene glycol-n-butyl ethers, propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, and dipropylene glycol methyl ether acetate), lactones (e.g., (gamma)butyrolactone, (epsilon)caprolactone, and (delta) dodecanolactone), alcohols and diols (2-methoxy-2-propanol, 1-octanol, 2-ethyl hexanol, cyclopentanol, 1,3 -propanediol, 2,3-butanediol, 2-methyl-2,4-pentanediol) and polydimethylsiloxanes (e.g., decamethyltetrasiloxane, decamethylpentasiloxane, and hexamethyldisiloxane), etc. Particularly suitable co-solvents include C₁-C₆ alcohols (e.g., methanol, ethanol, isopropanol, n-propanol), C₁-C₆ diols, methane, ethane, propane, butane, n-pentane, n-hexane, cyclohexane, n-heptane, ethylene, propylene, benzene, toluene, p-xylene, sulfur dioxide, chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, sulfur hexafluoride and nitrous oxide. The preferred co-solvent is a C₁-C₆ alcohol or diol. More preferably the co-solvent is a C₁-C₅ alcohol. Most preferably the co-solvent is a C₂-C₄ alcohol.

The aforementioned co-solvents are advantageously employed in an amount of at least 0.1 % by weight of the dry cleaning composition, more preferably in an amount of 0.1-10 % by weight.

As will be apparent to those skilled in the art, numerous additional ingredients can be included in the present fluid dry cleaning composition, including detergents, bleaches,

whiteners, softeners, sizing, starches, enzymes, hydrogen peroxide or a source of hydrogen peroxide, fragrances, etc.

The present method is suitably carried out at around room temperature. Hence, in a preferred embodiment the method comprises contacting the article with the fluid dry cleaning composition at a temperature between 0 and 30°C. Similarly, in a preferred embodiment step a) comprises contacting the article with the fluid dry cleaning composition at a pressure between 2 and 25 MPa.

In practice, in a preferred embodiment of the invention, the article to be cleaned and the fluid dry cleaning composition are combined in a closed drum. The liquid dry cleaning composition is preferably provided in an amount so that the closed drum contains both a liquid phase and a vapour phase (that is, so that the drum is not completely filled with the article and the liquid composition). The article is then agitated in the drum, preferably so that the article contacts both the liquid dry cleaning composition and the vapour phase, with the agitation carried out for a time sufficient to clean the article. The cleaned article may subsequently be removed from the drum.

The article may optionally be rinsed (for example, by removing the composition from the drum, adding a rinse solution such as liquid carbon dioxide (with or without additional ingredients such as water, co-solvent, etc.) to the drum, agitating the article in the rinse solution, removing the rinse solution, and repeating as desired), after the agitating step and before it is removed from the drum. The dry cleaning, compositions and the rinse solutions may be removed by any suitable means, including both draining, and venting.

In a particularly preferred embodiment of the invention, the present method comprises a rinsing step wherein the original dry cleaning composition is replaced by a composition containing densified carbon dioxide, and optionally other components, but no undissolved ionic surfactant. The latter composition may be used advantageously to remove any remaining undissolved surfactant. The rinsing operation with densified carbon dioxide may suitably be repeated several times. Preferably the densified carbon dioxide used in the rinsing operation contains a co-solvent as defined herein before and/or water, as such a co-solvent may facilitate the dissolving of the undissolved ionic surfactant and the water may enhance the removal of non-particulate soils.

Any suitable cleaning, apparatus may be employed, including both horizontal drum and vertical drum apparatus. When the drum is a horizontal drum, the agitating step is carried out by simply rotating the drum. When the drum is a vertical drum it typically has an agitator positioned therein, and the agitating step is carried out by moving, (e.g., rotating, or

oscillating) the agitator within the drum. A vapour phase may be provided by imparting sufficient shear forces within the drum to produce cavitation in the liquid dry-cleaning composition.

Finally, in an alternate embodiment of the invention, agitation may be imparted by means of jet agitation as described in U.S. Pat. No. 5,467,492 to Chao et al., the disclosure of which is incorporated herein by reference. As noted above, the fluid dry cleaning, composition is preferably an ambient temperature composition, and the agitating step is preferably carried out at ambient temperature, without the need for associating a heating, element with the cleaning apparatus.

The invention is further illustrated by means of the following examples.

EXAMPLES

Example 1

The experiment is carried out in a vessel of 25 litres with a rotating drum of 10 litres. The vessel has two viewing glasses to monitor the behaviour of the fluid. During the cleaning and rinsing cycle the rotating drum is alternately rotated clockwise for 30 seconds and counter clockwise for 30 seconds both at a speed of 75 cycles per minute. The dry-cleaning fluid is circulated over the vessel using a centrifugal pump. The piping from the vessel towards the pump contains a filter, while the piping from the pump towards the vessel contains a heat exchanger to control the temperature of the whole system. The equipment contains a mass flow meter, a temperature indicator and a pressure indicator.

During the cleaning cycle the rotating drum is filled with ten small pre-stained test fabrics. These stained test fabrics are:

	STAIN	FABRIC
1	sebum and carbon black	wool
2	sebum and carbon black	polyester
3	egg yolk	wool
4	egg yolk	polyester
5	butterfat with colorant	cotton
6	butterfat with colorant	polyester/cotton blend
7	vegetable oil with chlorophyll	cotton
8	vegetable oil with chlorophyll	polyester/cotton blend
9	clay	wool
10	clay	polyester

The test fabrics were attached to an additional load of 400 grams of white cotton fabrics. The stained test fabrics were analysed before and after the cleaning cycle to determine the coloration change of the fabrics. The values were expressed in Lab values. The absolute colour difference between two samples in the Lab space is expressed as:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}.$$

To examine the efficiency of the cleaning, both the cleaned and stained fabrics are compared with the original unstained fabric, leading to the absolute colour differences $\Delta E_{\text{stained-unsoiled}}$ and $\Delta E_{\text{cleaned-unsoiled}}$. The cleaning performance index of an experiment is expressed as:

$$CPI_{\text{Lab}} = \left(1 - \frac{\Delta E_{\text{cleaned-unsoiled}}}{\Delta E_{\text{stained-unsoiled}}} \right) \times 100\%$$

When the fabric is clean the CPI_{lab} value is 100%, when the cleaning has no effect the value is 0%.

The cleaning is started by filling the vessel at ambient conditions with the additional load and the attached stained test fabrics. Subsequently a cleaning fluid comprising of 250 grams of iso-propanol, 25 grams water and 39 grams of dissolved dodecylamine, was added to the fabric load. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glasses it was observed that a large amount of small particles is formed. The particles were collected and analysed. It was found that the material in the particles displayed a melting point that was about 20°C higher than the melting point of dodecylamine.

The rotating drum was started and the fabric is cleaned for 30 minutes. After the cleaning the vessel was rinsed with 12 kg of fresh carbon dioxide from the storage vessel for 10 minutes, while keeping the system at 48 bars. Subsequently the vessel was depressurised after which it was opened, the cleaned fabrics were taken out and the colour differences were measured. The CPI_{lab} values obtained are shown in the table below.

Example 2

Example 1 was repeated except that the cleaning fluid was composed of 250 grams iso-propanol, 25 grams water and 40 grams of dioctylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glass it was observed that a large amount of small particles was formed. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 3

Example 1 was repeated except that this time 50 grams of solid sodium stearate and 25 grams of water were put in the cleaning vessel. The vessel was closed and pressurised with 4 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 10 °C. Through the viewing glass it was observed that a large amount of sodium stearate did not dissolve in the carbon dioxide. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 4

Example 1 was repeated except that this time 10 grams of solid sodium dodecyl sulfate and 25 grams of water were put in the cleaning vessel. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 11 °C. Through the viewing glass it was observed that a large amount of sodium dodecyl sulfate did not dissolve in the carbon dioxide. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 5

Example 1 was repeated except that the cleaning fluid was composed of 250 grams of iso-propanol, 25 grams water and 1 gram of tribenzylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 45 bars and a temperature of 10 °C. Through the viewing glass it was observed that a large amount of small particles was formed. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 6

Example 1 was repeated except that the cleaning fluid was composed of 255 grams of iso-propanol, 25 grams water and 1 gram of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glass it was observed that small particles were formed. After the cleaning, the vessel was rinsed and depressurised

as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 7

Example 6 was repeated except that the cleaning fluid was composed of 251 grams of iso-propanol, 25 grams water and 5 grams of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 11 °C. Through the viewing glass it was observed that small particles were formed. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 8

Example 6 was repeated except that the cleaning fluid was composed of 250 grams of iso-propanol, 25 grams water and 10 grams of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 48 bars and a temperature of 12 °C. Through the viewing glass it was observed that a substantial amount of small particles was formed. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 9

Example 6 was repeated except that the cleaning fluid was composed of 250 grams of iso-propanol, 30 grams water and 40 grams of octadecylamine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 46 bars and a temperature of 11 °C. Through the viewing glass it was observed that a large amount of small particles was formed. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 10

Example 1 was repeated except that the cleaning fluid was composed of 250 grams of iso-propanol and 10 grams of N-Lauroyl-L-lysine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 57 bars

and a temperature of 20 °C. Through the viewing glass it was observed that a large amount of small particles was formed. After the cleaning, the vessel was rinsed and depressurised as described in Example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

Example 11

Example 1 was repeated except that the cleaning fluid was composed of 250 grams of iso-propanol and 5 grams of N-Lauroyl-L-lysine. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 52 bars and a temperature of 16 °C. Through the viewing glass it was observed that a large amount of small particles was formed. After the cleaning, the vessel was rinsed with pure carbon dioxide and depressurised as described in Example 1. Subsequently a rinsing fluid comprising of 250 grams of iso-propanol and 25 grams water was added to the fabric load. The vessel was closed and pressurised with 6 kg of liquid carbon dioxide from a storage tank. The rotating drum was started and the fabric was rinsed for 30 minutes. After this rinsing step, the vessel was rinsed again with pure carbon dioxide and depressurised as described in Example 1.

Comparative example A

Example 1 was repeated except that no cleaning liquid was put in the vessel. The vessel was closed and pressured with 12 kg of liquid carbon dioxide from a storage tank. The system reached a pressure of 45 bars and a temperature of 10 °C. After the cleaning, the vessel was rinsed and depressurised as described in example 1. The CPI_{lab} values found for each of the test fabrics are shown in the table below.

The cleaning performance (expressed as CPI_{lab} values) achieved in each of the cleaning cycles described in the aforementioned examples is summarised in the following table:

	EXAMPLES											
	1	2	3	4	5	6	7	8	9	10	11	A
Sebum on wool	74	76	63	58	44	55	57	79	89	71	72	30
Sebum on polyester	46	44	44	40	23	36	42	48	58	49	56	21
Egg-yolk on wool	64	62	46	47	56	60	60	62	64	44	56	41
Egg-yolk on polyester	50	55	40	38	49	51	48	49	53	40	39	37
Butterfat on cotton	80	90	72	62	88	84	86	86	84	75	91	65
Butterfat on blend fabric	87	93	83	76	92	89	89	90	87	83	94	80
Vegetable oil on cotton	57	67	41	27	64	55	51	61	65	49	54	16
Vegetable oil on blend fabric	20	20	27	19	26	22	15	24	23	22	20	6
Clay on wool	68	62	52	66	32	43	35	44	47	71	83	13
Clay on polyester	12	11	27	39	2	13	9	2	12	16	17	1

The above results show that the addition of an ionic surfactant dramatically improves the cleaning performance. The examples 1, 2, 3, 4, 5, 9, 10 and 11 illustrate that the benefits of the present invention may be obtained with different types of ionic surfactants, even though the improved cleaning performance may manifest itself in different ways. The results also shown that the amines are particularly effective. The examples 6, 7, 8 and 9 show that an increase of the concentration of the surfactant increases the cleaning performance of the washing cycle. This is a surprising finding since the applied amount of dissolved surfactant is the same in all these samples. All examples show that especially the removal of particulate soils is improved dramatically.

CLAIMS

1. A method of dry cleaning an article, especially fabric, comprising the successive steps of:

a) contacting the article with a fluid dry cleaning composition containing densified carbon dioxide at a temperature between -20 and 60°C and a pressure between 1 and 100 MPa, so as to allow stains to dissolve and/or to disperse into the fluid dry cleaning composition and

b) separating the article and the fluid dry cleaning composition;

wherein the fluid dry cleaning composition comprises ionic surfactant in a concentration of between 0.01 and 15% by weight of the carbon dioxide and wherein during step a) at least 10%, preferably at least 30% of said ionic surfactant is present in an undissolved solid form.

2. The method according to claim 1, wherein the duration of step a) exceeds 1 minute, preferably 2 minutes.

3. The method according to claim 1 or 2, wherein the ionic surfactant contains one or more lipophilic hydrocarbyl residues with 3-25 carbon atoms and one or more groups selected from amine, phosphate, phosphonate, phosphinate, phosphonite, phosphine, phosphinite, phosphite, quaternary phosphonium salt, quaternary ammonium salt, sulphate, sulphonate, sulphinate, sulphenate, sulphide and carboxylate groups.

4. The method according to any one of claims 1-3, wherein the ionic surfactant is represented by the formula R_1X , XR_1X , R_2YR_2' , $R_3Z(R_3')R_3''$ or $R_3E(R_3')(R_3'')R_3'''D$; wherein:

R_1 is a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkyl; a substituted or unsubstituted, optionally heterogeneous C_3 - C_{16} cycloalkyl; a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;

R_2 and R_2' independently are R_1 , X , R_aX or $R_a(X)_2$;

R_3 , R_3' , R_3'' and R_3''' independently are R_1 , X , R_aX , YR_1 , $R_a(YR_a)_nYR_1$ or $Y(R_aY)_nR_1$;

R_a is a substituted or unsubstituted, linear or branched, optionally heterogeneous C_1 - C_{22} alkyl; a substituted or unsubstituted, optionally heterogeneous C_3 - C_{16} cycloalkyl; a substituted or

unsubstituted, linear or branched, optionally heterogeneous C₁-C₂₂ alkenyl; or a substituted or unsubstituted, optionally heterogeneous aryl;

and wherein

X is NH₂, NH₃⁺, OP(O)(OM₁)(OM₂), OP(O)₃²⁻Q²⁺, P(O)(OM₁)(OM₂), P(O)₃²⁻Q²⁺,

P(O)(H)(OM₁), OS(O)₂(OM₁), S(O)₂(OM₁), S(O)(OM₁), COO⁻ or COOM₁;

Y is NH, NH₂⁺, OP(O)(OM₁)O, P(O)(OM₁)O, P(O)(OM₁), OS(O)₂O, S(O)₂O, S(O)O;

Z is N, NH⁺;

E is N⁺;

D is F⁻, Cl⁻, Br⁻ or I⁻;

M₁ and M₂ independently represent sodium, potassium, ammonium or hydrogen;

Q²⁺ represents Ca²⁺, Cu²⁺, Mg²⁺ or Zn²⁺; and

n = 0-20.

5. The method according to claim 4, wherein the ionic surfactant is represented by the formula R₁X, XR₁X, or R₂YR₂, wherein X is NH₂, NH₃⁺, COOM₁, COO⁻, OP(O)(OM₁)(OM₂), OS(O)₂(OM₁) and Y is NH.

6. The method according to claim 4, wherein R₁ and R_a independently are a substituted or unsubstituted, linear or branched, optionally heterogeneous C₃-C₂₂ alkyl or are a substituted or unsubstituted, linear or branched, optionally heterogeneous C₃-C₂₂ alkenyl.

7. The method according to any one of claims 1-6, wherein the fluid dry cleaning composition contains between 0.0001 and 5 wt.% water.

8. The method according to any one of claims 1-7, wherein the fluid dry cleaning composition contains a co-solvent selected from the group consisting of aliphatic and aromatic hydrocarbons, and esters and ethers thereof, alkyl and dialkyl carbonates, alkylene and polyalkylene glycols, and ethers and esters thereof, lactones, alcohols and diols, polydimethylsiloxanes and combinations thereof.

9. The method according to any one of claims 1-8, wherein step a) comprises contacting the article with the fluid dry cleaning composition at a temperature between 0 and 30°C.

10. The method according to any one of claims 1-10, wherein step a) comprises contacting the article with the fluid dry cleaning composition at a pressure between 2 and 25 MPa.

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00788

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 D06L1/00 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 676 705 A (JURELLER ET AL) 14 October 1997 (1997-10-14) column 3, line 59 - line 64 column 19, line 45 - line 48 claims 1,2	1-10
X	US 5 858 022 A (ROMACK ET AL) 12 January 1999 (1999-01-12) column 2, line 7 - line 9 column 2, line 62 - line 64 examples 1,2 claims 19,20,26	1-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

16 June 2003

Date of mailing of the international search report

08/07/2003

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